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Description

5 Piezoelectric Device

The invention concerns a piezoceramic device with a stack of at least two ceramic layers and an electrode layer arranged between two ceramic layers and a method to its production.

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Such piezoceramic devices therefore include several, particularly many layers (multilayer devices); they are for example utilizable as actuators in piezo stacks, by obtaining a low-inertia mechanical excursion of comparably high force by the voltage control or as bending elements, by causing a high mechanical excursion of less force by the voltage control, or they permit the production of high electrical voltages resp. serve the detection of mechanical or the production of acoustic vibrations with the relevant devices.

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Technical solutions up to now are based on predominantly ceramic masses of the Perovskite structure type of the general formula ABO_3 , whereby the piezoelectrical characteristics are brought to bear in the ferroelectrical condition. Lead

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zirconate titanate ceramics $Pb(Zr_{1-x}Ti_x)O_3 = PZT$ modified by certain additives, have been shown particularly advantageous, whose combination is tailored to the so-called morphotropic phase interface of two co-existing ferroelectrical phases, a tetragonal and a rhombodic phase. Between the ceramical

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layers, produced according to the typical methods of the ceramic foil technology, there are precious metal internal electrodes applied by screen printing, for example Ag/Pd in the molar ratio 70/30. At up to several hundred electrode layers, the devices are thereby burdened with substantial

costs. The precious metal electrodes permit to eliminate thermically the dispergers and binders as well as the other organic additives used in the process of the ceramic foil production, and also the organic components of the screen printing-metal paste of the multilayer stacks by air depolymerisation and oxidation, so that afterwards a sinter condensation at approx. 1100 to 1150°C is made possible, without causing reduction effects, for example conditioned by residue carbon left-overs, which negatively influence the characteristics of the ceramics because of reduction reactions.

Tests with La_2O_3 or Nd_2O_3 doped $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ - ceramics are particularly documented in the literature, for example of G.H. Haertling in the journals American Ceramic Society Bulletin (43(12), 113-118 (1964) and Journal of the American Ceramic Society 54, 1-11 (1971) as well as in the monographics "Piezoelectric Ceramics", Academic Press, London and New York (1971) of B. Jaffe, W.R. Cook and H. Jaffe as well as of Y. Xu. In "Ferroelectric Materials and their Applications", Elsevier Science Publishers, Amsterdam (1991).

La_2O_3 - resp. Nd_2O_3 - additives induce the production of cation vacancies on the Pb positions of the crystal structure, but at the same time increase thereby the tendency to act as donors, particularly at insufficient oxygen partial pressure, which can lead to a depression of the insulating resistance and a rise of the dielectrical losses, i.e. the sensitivity of the ceramic towards reduction is increased. At the same time they stabilize the tetragonal phase, and the kinetics of the orientation of the domains in field direction at the polarity are facilitated, i.e. the electro mechanical characteristic behavior of a so called "soft piezoceramic" is influenced positively by such additives for this application. For an

advancement of the sinter condensation and prevention of evaporation losses at PbO of the ceramic, a low PbO surplus at the originally weighed-in composition is generally considered. It was talked in detail about the connection between the
5 doping level by La_2O_3 in a $\text{Pb}(\text{Zr}_{0.47}\text{Ti}_{0.53})\text{O}_3$ -ceramic supplied with 3 molar-% PbO surplus and the sinter behavior as well as the structure formation associated with this and the electro magnetic characteristics like coupling factor and dielectricity constant including the curie temperature, the
10 maximum temperature for ferroelectrical and with it also piezoelectrical behavior, in the journal of electroceramics 2(2), 75-84 (1998) by M. Hammer and M. Hoffmann.

Ceramic masses with bismuth oxide in place of lead oxide were
15 also taken into consideration, for example $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - KNbO_3 - BiScO_3 of T. Takenaka, H. Nagata in proceedings of the 11th Inter. Symp. Appl. of Ferroelectrics, Montreux 1998, IEEE 98CH36245, 559-562 (1998), or $\text{Pb}(\text{Ti}_x\text{Zr}_{1-x})\text{O}_3$ was combined with BiScO_3 and/or BiInO_3 . All these ceramics are based on
20 Perovskite mixed crystal phases, which in combination with Ag/Pd internal electrodes produce a relatively positive characteristic behavior for the purpose of piezo stack, when the debinding, i.e. the removal of the binder or binders, and the sinter condensation is air-done.

25 Piezoelectrical ceramic masses of the general composition $(\text{Pb}_{1-x-\alpha-y}\text{Sr}_x\text{Na}_\alpha\text{M}_y)_a\{(\text{Nb}_b\text{Y}_c\text{Cr}_d\text{Co}_e\text{Sb}_\beta)_f\text{Ti}_g\text{Zr}_{1-f-g}\}\text{O}_3$ are protected in the print US 5 648 012, which are distinguished by high electromechanical coupling factors, whereby M is at least a
30 rare earth metal of La, Gd, Nd, Sm and Pr and the parameter areas $0.005 \leq x \leq 0.08$, $0.002 \leq y \leq 0.05$, $0.95 \leq a \leq 1.105$, $0.47 \leq b \leq 0.70$, $0.02 \leq c \leq 0.31$, $0.11 \leq d \leq 0.42$, $0.01 \leq e$

≤ 0.12 , $0.02 \leq f \leq 0.15$, $0.46 \leq g \leq 0.52$, $0 \leq \beta \leq 0.13$ as well as $b+c+d+e+\beta=1.00$ are known.

The print DE 9700463 for the production of green foils for
5 piezoceramic multilayer devices is as well based on a
piezoceramic powder of the type PZT, to which a stoichiometric
surplus of a heterovalent rare earth metal up to a content
from 1 to 5 molar-% and a stoichiometric surplus of an
additional 1-5 molar-% lead oxide is added. In addition it is
10 documented in this print, that Ag^+ - ions from the area of
 Ag/Pd - internal electrodes diffuse exactly in such a portion
into the ceramic layers of the multilayer devices, that the by
the heterovalent doping produced cation vacancies are occupied
and in this way will result in a filled up Perovskite
15 structure, like for example
 $Pb_{0.99}Ag_{0.01}La_{0.01}\{Zr_{0.30}Ti_{0.36}(Ni_{1/3}Nb_{2/3})_{0.34}\}O_3$ or
 $Pb_{0.96}Ag_{0.02}Nd_{0.02}(Zr_{0.54}, Ti_{0.46})O_3$. In the latter case a
piezoceramic is produced with a comparatively high Curie
temperature for applications up to $150^\circ C$. It is also well
20 founded that the composite solidity between the Ag/Pd internal
electrode (70/30) and the ceramic as well as the corn growth
at the sintering are positively influenced by building silver
into the ceramic.

25 To prevent the disadvantage of the high costs of such
piezoceramic multilayer elements on the basis of a ceramic of
a PZT-type, it is possible, to provide an application of
copper in place of the expensive Ag/Pd - internal electrodes.
Thermodynamic data has shown, that PZT-ceramic is for example
30 at $1000^\circ C$ under a certain very low oxygen partial pressure of
 $< 10^{-2}$ is not reduced and metallic copper stays under these
conditions stable as well, i.e. doesn't oxidize.

That this statement is also accurate on a donor doped ceramic, is proven by an examination of Cao and employees in the journal of the American Ceramic Society 76(12) 3019 (1993), wherein Cu foil is laid between pre-made ceramic segments

- 5 $\text{Pb}_{0.988}(\text{Nb}_{0.024}\text{Zr}_{0.528}\text{Ti}_{0.473})\text{O}_3$ and such a multiple sandwich arrangement is subject to an examination to a sintering at 1050°C under vacuum. The good composite between the ceramic and Cu internal electrode and the absence of the migrational effects, like they are observed at Ag electrodes on air, are
- 10 emphasized. But such a way of process does not correspond to the requirements of an efficient production, like the foil multilayer technology makes it possible, and is not apt for a mass production.
- 15 Kato and colleagues describe in Ceramic Transactions Vol. 8, pages 54-68 (1990) the production of multilayer condensators with Z5U specifications on the basis of ceramics of the general formula $(\text{Pb}_a\text{-Ca}_b)(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y(\text{Ni}_{1/2}\text{W}_{1/2})\text{Zr}_{0.5}\text{O}_{2+a+b}$ ($a+b>1$, $x+y+z=1$) with Cu internal electrodes, whereby a copper oxide
- 20 screen-printing paste is used. Air-debinding is thereby made possible. The carbon formation, which would inevitably come into effect under nitrogen at a well-tolerated metallic copper with oxygen partial pressure and afterwards at the sinter condensation lead to a reductive degradation of the ceramic
- 25 with Cu/Pb -alloying production - the eutectic melting point lies at $T_S = 954^\circ\text{C}$ - is thereby avoided. After the debinding, the sinter condensation is then carried out at 1000°C by additional dosage of hydrogen at a oxygen partial pressure, 10^{-3} Pa and the copper oxide is reduced to copper
- 30 under these conditions. The process is interference-prone because of the shrinkage during the reduction from copper oxide to copper and the from this resulting tendency to delamination and has up to now not been technologically converted into products.

In the print DE 197 49 858 C1, at the production of COG - multilayer condensators with Cu - internal electrodes on the basis of a ceramic mass with the general composition $(\text{Ba}^{\text{II}}_{1-y}\text{Pb}_y)_{6-x}\text{Nd}_{8+2x/3}\text{Ti}_{18}\text{O}_{54} + z \text{ m-\% TiO}_2 + p \text{ m-\% Glas}$ at lower PbO content ($0.6 < x < 2.1$; $0 < y < 0.6$, $0 < z < 5.5$ and $3 < p < 10$) a sufficient elimination of the organic components by feeding steam into the nitrogen flux with $< 10^{-2}$ Pa oxygen partial pressure at temperatures up to 680°C and the sinter condensation at 1000°C is reached by apt glass frit additives. The method could be successfully applied in the DE 19841487 on COG-multilayer condensators with the PbO free ceramic $\text{Ba}^{\text{II}}_{6-x}(\text{Sm}_y\text{Nd}_{1-y})_{8+2x/3}\text{Ti}_{18}\text{O}_{54} + p \text{ weight -\% glass frit}$ ($1 < x < 2$, $0.5 < y < 1.0$ and $3 < p < 1$).

Piezoceramic devices in a monolithic multilayer built with Cu-containing internal electrodes on the basis of a piezoceramic of any composition, preferably on the basis of a Perovskite ceramic of the PZT type are intended according to the invention. The modification by mixed crystal formation by building in cations on the-A positions as well as by substitution of the B-cations by apt other cations or combinations of cations can be thereby achieved, and the from the production of multilayer condensators known methods of ceramic foil technique as well as the common sintering of the ceramic layers with the for example by screen printing alternatively brought in Cu-internal electrodes can be applied.

Such piezoceramic multilayer devices can be realized for example as actuators by an apt process guide, by which the debinding of the green foil stacks is carried out without adding oxygen, which would oxidize the Cu-internal electrodes and the following sinter condensation to a monolithic

multilayer device can come about at already 1000°C, this means below the melting temperature of the copper.

Advantageous further formations are separately marked.

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The advantage of the invention lies therein, that for a PZT ceramic mass, Cu-internal electrodes are applied in place of the so far normally used Ag/Pd internal electrodes (70/30) on the basis of the multilayer foil technique, whereby the
10 practically complete debinding can be successfully done before inserting the sinter condensation without using oxygen, i.e., under inert conditions in such a way that a lot of steam is supplied to the oxygen atmosphere during the debinding and permits only a set minimum oxygen partial pressure of 10^{-3}
15 to 10^{-1} Pa, which leaves the Cu-internal electrodes intact. Thereby the conditions are being created, that during the process of the following sinter condensation, piezoactuators with optimal characteristical results of the ceramic can be obtained, which don't take second place to the ones which were
20 under analogue conditions separated from the Cu-electrode layer or also air-sintered piezo ceramic layer of the corresponding composition resp. do even better.

The invention includes the realization, that the by donors,
25 for example, a rare earth metal, doped piezo ceramic on the basis of PZT because of the formation of cation vacancies on the A-positions of the Perovskite structure, for example according to the composition $\text{Pb}^{\text{II}}_{0.97} \text{Nd}^{\text{III}}_{0.02}$
 $\text{V}''_{\text{Pb},0.01}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$, develops a certain affinity, to absorb
30 copper from the internal electrodes, without destroying them, exactly to a critical concentration, which results from the concentration of the cation vacancy and the elimination of equivalent PbO-shares, whereby the latter combination acts as

a sinter aid and up to some percentage of PbO is separately added to the ceramic anyway.

The sinter condensation and the grain growth is supported by the known mobility of the copper ions to average diameter of 1 to 5 μm , and leads by the copper migration to a solid adhesion between the electrode layer and ceramic, so that delaminations can be effectively avoided this way.

With the penetration of copper into the PZT-ceramic layer, an advantageous increase of the Curie-temperature by 80 to 100 $^{\circ}\text{C}$ to 420 to 440 $^{\circ}\text{C}$, which has an advantageous effect on the operational safety of thusly fabricated piezo-ceramic multi-layer components with Cu-internal electrodes under the conditions of an increased thermal stress, for example, of piezo-stacks in the temperature region of up to 150 or even 200 $^{\circ}\text{C}$, as compared to the previously known technical solutions of an multi-layer ceramic component sintered on air with Ag/Pd internal electrodes.

It is thus of advantage, to already add some CuO within the limits $0 < y < 0.15$ to the original mixture of the used recipe for piezo stacks for example on the basis of PZT with Cu-internal electrodes corresponding to the general formula $\text{Pb}^{\text{II}}_{1-x-y}\text{SE}^{\text{III}}_x\text{Cu}^{\text{II}}_y\text{V}''_{x/2}(\text{Zr}_{0.54-z}\text{Ti}_{0.46+z})\text{O}_3$ with $0.005 < x < 0.05$ and $-0.15 < z < +0.15$ (SE = Rare Earth Metal). The Curie-temperature can thereby be purposefully increased, whereby the piezoelectrical characteristics, like the high value for the electromechanical coupling factor can be maintained at corresponding adjustment of the parameter z to the morphotropic phase interface.

The invention is explained in more detail by the following models and four figures belonging to them.

The from TiO_2 , ZrO_2 resp. from a mixed precipitation produced precursor $(\text{Zr}, \text{Ti})\text{O}_2$ and PbCO_3 resp. Pb_3O_4 and dopants like La_2O_3 or from another oxide of the rare earth metals and if
5 necessary an additive of CuO based raw material mixture is set in its composition on the morphotropic phase interface, a PbO -surplus of maximally 5 % to support the sinter condensation and a set Curie-temperature, for even distribution of the component undergoes a grinding step in diluted suspension an
10 is calcinated after the filtering and drying at 900 to 950°C . Thereby the piezoceramic Perovskite-mixed crystal phase is built. To obtain sinter condensation in 2 to 4 hours at already 1000° below the melting temperature of copper, a pulverization to a medium grain size $< 0.4\mu\text{m}$ is necessary. The
15 sinter activity of the powder shows then to be sufficient, to guarantee a condensation of $> 96\%$ of the theoretical density at both sufficient grain growth and adequate mechanical solidity in the ceramic structure.

20 The finely ground powder is suspended to a diluted slip with approx. 70 m-% solid substance content by use of a disperger, this corresponds to approx. 24 vol.-%. For this, the for an optimal dispersing just necessary dispergator portion is separately determined in a series of tests, which can be
25 recognized by obtaining a viscosity minimum. Approx. 6 m-% of a binder is added to the dispersed suspended solids, which is thermohydrolytically degradable, for the formation of the piezo-ceramic green foils, mixed in a disperse mill and receives this way a for the process of "foil-pulling" resp.
30 for the production of a spraying granular apt slip.

Discoid green compacts, produced from the granular, or small square multilayer printed boards "MLP", produced by stacking and laminating from the 40 to 50 μm thick green foils without

print with Cu-electrode paste, can be debindered up to a residue carbon content of 300 ppm in a H₂O-steam containing nitrogen atmosphere at a defined oxygen partial pressure, which fulfills the condition of the coexistence of PbO resp.

5 Bi₂O₃-containing piezoceramic and copper.

Figure 1 shows the temperature control during the debinding. The steam partial pressure supplied with the nitrogen flux corresponding to a dew point of 80°C is indicated as well.

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At such debindered PZT-ceramic samples the sinter condensation is succeeded at 1000°C, without creating a reductive degradation of the ceramic. The dielectrical and especially the piezoelectrical characteristics of the obtained samples with the measurements of approx. 10.10 mm² and 0,7 resp. 2 mm consistency are measured after contacting by sputtering of Au-electrodes and compared with the air-debindered and at 1130 °C sintered samples of the same geometry.

20 For air-sinterings of ceramic samples MLP without internal electrodes with the composition

Pb^{II}_{0.97}Nd^{III}_{0.02}V^{'''}_{0.01}(Zr_{0.54} Ti_{0.46})O₃ and under inert conditions, whereby the latter correspond to the requirements of a common sintering with copper, the results of the electrical measuring are compiled in table 1, the ones of the polarized samples in table 2.

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Table 1: Characteristics of square ceramic samples MLP (edge length l, thickness d) with the composition Pb^{II}_{0.97}

30 Nd^{III}_{0.02}V^{'''}_{Pb,0.01}(Zr_{0.54} Ti_{0.46})O₃. (a) powder pre-ground to a medium grain size d_{50%}=0.53 µm, air-sintering at 1120°C; (b) and (c) powder finely ground to a medium grain size d_{50%}=0.33 µm, air-sintered (b) at 1000°C resp. (c) at 1000°C under N₂/H₂O-steam.

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Sample MLP	d/mm	l/mm	C/μF	ε	Tan δ	R _{IS} /Ω	ρ/Ωcm
(a)	0.59±0.02	10.8±0.1	2200±50	1268±30	2.1±0.1%	1*10 ¹¹	2*10 ¹²
(b)	0.70±0.01	10.6±0.1	1600±30	1137±58	2.8±0.2%	2*10 ¹¹	3*10 ¹²
(c)	0.71±0.02	11.0±0.8	1620±70	1132±81	2.8±0.6%	5*10 ⁹	9*10 ¹⁰

Table 2: Characteristics of square ceramic samples MLP (edge length l, thickness d) with the composition Pb^{II}_{0.97}

5 Nd^{III}_{0.02}V''_{Pb,0.01}(Zr_{0.54}Ti_{0.46})O₃ according to table 1 after the polarity with 1200 V (a) resp. 1400 V(b) and (c).

Sample MLP	h/mm	l/mm	C/μF	ε	Tan δ□	R _{IS} /Ω	ρ/Ωcm
(a)	0.59±0.02	10.8±0.1	2540±130	1460±134	1.9±0.1%	1*10 ¹¹	2*10 ¹²
(b)	0.70±0.01	10.6±0.1	170±30	1207±58	2.1±0.1%	1*10 ¹¹	2*10 ¹²
(c)	0.71±0.02	11.0±0.8	1750±50	1238±69	2.3±0.1%	2*10 ¹¹	5*10 ¹²

10 The characteristic values prove, that PZT ceramic samples, which were not air-bindered and were sintered, show comparable dielectrical characteristics.

15 The results of table 3 are based on electromechanical vibration measuring with the aid of an impedance measuring bridge, whose evaluation from the parallel and serial resonance frequency f_p , f_s of the resonant circuit according

$$f_s = \frac{1}{2\pi} \cdot \sqrt{\frac{1}{C_1 \cdot L_1}}$$

$$f_p = \frac{1}{2\pi} \cdot \sqrt{\frac{C_0 + C_1}{C_0 \cdot C_1 \cdot L_1}}$$

20 permits to calculate for each vibration mode of the MLP sample of the effective coupling factor according

$$K_{eff}^2 = \frac{f_p^2 - f_s^2}{f_p^2} = \frac{\frac{C_0 + C_1}{C_0 \cdot C_1 \cdot L_1} - \frac{C_{01}}{C_0 \cdot C_1 \cdot L_1}}{\frac{C_0 + C_1}{C_0 \cdot C_1 \cdot L_1}} = \frac{C_1}{C_0 + C_1}$$

Thereby, the proportion of the mechanical energy for the entire energy is indicated by $C_1/(C_0+C_1)$.

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Table 3: Effective piezoelectrical coupling factors of the MLP samples from table 2 for two fundamental vibrations, determined from the measurement of each 3 MLP samples, sintered under the indicated conditions (a), (b), (c) and (d) in table 1.

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MLP	Planar vibration			Consistency mode of vibration		
	f_s/kHz	f_p/kHz	k_{eff}	f_s/kHz	f_p/kHz	k_{eff}
(a)	158 \pm 1	191 \pm 2	0.56 \pm 0.01	3293 \pm 15	3848 \pm 79	0.52 \pm 0.03
(b)	166 \pm 2	198 \pm 4	0.54 \pm 0.01	2900 \pm 78	3197 \pm 25	0.42 \pm 0.05
(c)	163 \pm 1	189 \pm 5	0.51 \pm 0.04	2830 \pm 111	3100 \pm 108	0.40 \pm 0.02

The measurement of the Curie temperature at samples (c) showed a value of $339 \pm 2^\circ\text{C}$.

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In fact, electromechanical coupling factors, which are in the area of the air-sintered samples, are accrued from the produced samples, sintered commonly under these conditions with copper.

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In case of printing on Cu-internal electrodes, a Cu-screen print paste proves to be advantageous, which shows a metal content as high as possible of approx. 75 m-% and is processed with a special high-polymer and thereby very viscous binder, which produces at already < 2m-%, related to the solid substance content, a viscosity as thixotrope as possible of > 2000 mPa.s. First, multilayer samples "VS" with up to 20

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internal electrodes are produced for sample purposes. Starting from this, piezo stacks with 100 to 300 Cu-internal electrodes are built up in a second step and are debindered and sintered under the mentioned conditions of a defined oxygen partial pressure in presence of steam.

The piezoceramic green foils are produced in a consistency, which produces, by considering the linear shrinkage during the sintering of typically 15%, a piezoceramic consistency from 20 to 200 μm . The Cu-electrodes have a layer consistency from 1 to 3 μm after the sintering.

Figure 2 shows partially a schematic cross section by a multilayer stack with alternating sequence of PZT ceramic foils and Cu-internal electrodes.

Figure 3 shows a measuring curve for the Cu-content of a piezoceramic layer about the layer consistency after the sintering of a piezo stack on the basis of the used original composition

$\text{Pb}^{\text{II}}_{0.97-y}\text{Nd}_{0.02}\text{Cu}^{\text{II}}\text{yV}^{\text{' ' '}}_{0.01}(\text{Zr}_{0.54-z}\text{Ti}_{0.46+z})\text{O}_3$. It can be seen that the copper content in the ceramic layer, starting from the border, decreases to the minimum amount of $y=-.001$, but that it increases to approximately 20 times higher values at the borders. The calibration produces in the middle of the ceramic layer the minimal amount of $y = 0.001$. Some lead oxide is displaced from the combination by the into the Cu-ions diffused influence. The good connection of the Cu-internal electrodes to the ceramic is thereby proven.

The electrical characteristics of the multilayer ceramic components VS of the original composition

$\text{Pb}^{\text{II}}_{0.97}\text{Nd}^{\text{III}}_{0.02}\text{V}^{\text{' ' '}}_{0.01}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$ after the sintering at 1000°C with 16 Cu-internal electrodes and for comparison with 20

Ag/Pd-internal electrodes (70/30) after the air-sintering at 1120°C are indicated in table 4.

The advantageous increase of the Curie-temperature to 415 or 440°C takes place due to the contamination of copper from the interior electrodes during the sintering.

Table 4: Electrical characteristics of PZT multilayer ceramic samples VS on the basis of the original composition

10 $\text{Pb}^{\text{II}}_{0.97}\text{Nd}^{\text{III}}_{0.02}\text{V}^{\text{III}}_{0.01}(\text{Zr}_{0.54}\text{Ti}_{0.46})\text{O}_3$: (a) powder pre-ground, medium grain size $d_{50\%}=0.53 \mu\text{m}$, 20 internal electrodes Ag/Pd (70/30), air-sintering at 1120°C, (c) powder finely ground, medium corn size $d_{50\%}= 0.33 \mu\text{m}$, 16 Cu-internal electrodes, sintering at 1000°C under inert conditions by $\text{N}_2/\text{H}_2\text{O}$ steam.

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Sample VS	Comments	C/pF	ϵ before polarization	ϵ after polarization	$T_c/^\circ\text{C}$	$\tan \delta$ after polarization	$\rho_{\text{IS}}/\Omega\text{cm}$ after polarization
(a)	Ag/Pd(70/30: Debinding/air-sintering 1120°C, Cu-finished.	125 \pm 5	1104 \pm 54	1561 \pm 92	339	0.015	79 10^{11}
(c1)	Cu-internal electrodes: Debinding/sintering under $\text{N}_2/\text{H}_2\text{O}$ steam, Cu-finished.	110 \pm 4	908 \pm 35	953 \pm 37	415	0.027	2.7 10^{10}
(c2)	Cu-internal electrodes: Debinding/sintering under N_2 , H_2O steam, Cu-finished.	114 \pm 4	946	1013	440	0.026	1.6 10^{10}

Production of a piezo actuator from a ceramic of PZT type with Cu-internal electrodes.

For the production of piezo actuators with at first 160 Cu-
5 internal electrodes, the green foils produced according to the method of the consistency from 40 to 50 μm are further processed according to the for multilayer ceramic condensators known standard method. The printing of the square cut PZT ceramic foils is done mechanically by screen printing
10 technique (400 mesh) with the for piezo actuators common electrode design by usage of a commercial Cu-electrode paste. The stacking is done in a way, so that on each two non-printed foils a printed one follows. 100 piezo actuators in a green condition are received from the block after laminating by
15 pressing or sawing.

The debinding is carried out corresponding to the in figure 1 shown temperature time diagram in the nitrogen stream by adding steam and hydrogen, so that there is a target value
20 from $5 \cdot 10^{-2}$ to $2 \cdot 10^{-1}$ Pa produced in the area of 500°C . Essentially lower oxygen partial pressures occur locally during the debinding. The ceramic is not subject to the reductive degradation in the temperature area of the debinding, because the equilibrated oxygen partial pressure
25 is as well lowered, conditioned thermodynamically, and the reduction processes are kinetically sufficiently obstructed. The green parts of the multilayer piezo actuators still show a residue content of carbon of 300 ppm after the debinding and are immediately afterwards ready to be sintered in the same
30 set atmosphere, without causing a reductive degradation, which would lead to cracking, delamination and eventually to drifting of the internal electrodes because of the production of a low melting Cu/Pb-alloy. In the steam/nitrogen-oxygen atmosphere, the carbon content in the piezo-actor is reduced

during the sintering at 1000°C in 2 to 4 hours to approximately 20 ppm.

Intact crack-free actuators are obtained. Their sequence of the internal electrodes and PZT ceramic layers is shown in a section in figure 2. The medium grain size in the ceramic structure is $d_{50} = 1.6 \pm 0.3 \mu\text{m}$. It lies thereby in a for the formation of piezoelectrical active domains advantageous area.

10 The piezo actuators are ground and polished for the finishing and contacted in the area of the exiting internal electrodes with a for such applications common Cu-paste and burned-in at 935°C according to a preset temperature time curve. The piezo actuators respond to the electrical measuring after the
15 application of wires by the common Bond-technology.

The diagram of an excursion curve for a polarized PZT-piezoactuator with 160 Cu-internal electrodes is represented in figure 4. A density of 0,123% is produced by a voltage
20 setting of 140.6 Volt at a consistency of 70 μm of the PZT ceramic layers. The piezoelectrical coefficient in direction to the applied field d_{33} is $614.6 \cdot 10^{-12}\text{m/V}$.

Patent Claims

1. Piezoceramic device with a stack of at least two ceramic layers and an electrode layer set in between two ceramic layers,
5 characterized in that the electrode layer contains copper.
2. Piezoactor in monolithic multi-layer design with Cu-
10 interior electrodes on the basis of a ferroelectric Perovskite-ceramic ABO_3 , particularly of the PZT-type $Pb(Zr_xTi_{1-x})O_3$,
characterized in that
a modification by mixed crystal formation by the assembly of
15 cations is provided on the A-positions as well as by substitution of the B-cations by suitable other cations or by combinations of cations.
3. The piezoactor according to claim 2,
20 characterized in that
for the substitution on the A-positions of the ferroelectric Perovskite-ceramic, mainly of PZT type, bivalent metal cations M^{II} , such as Ba, Sr, Ca, Cu, or Bi or as rare earth metal Sc, Y, La, of one of the Lanthanide elements which follow in the
25 periodic system or any combination of these elements is used and/or a combination with monovalent cations, such as Ag^I , Cu^I , Na^I or K^I is provided.
4. The piezoactor according to claims 2 or 3,
30 characterized in that
for the partial substitution of the quadrivalent cations Zr and Ti on the B-positions of the ferroelectrical Perovskite ceramic, mainly of PZT-type, combinations of mono- and quintvalent metal cations $M^{I}_{1/4}M^{V}_{3/4}$ with $M^I = Na, K$ and $M^V = Nb,$

Ta or bi- and quintvalent metal cations $M^{II}_{1/3}M^V_{2/3}$ with $M^{II} = \text{Mg, Zn, Ni, Co}$ and $M^V = \text{Nb, Ta}$ or tri- and quintvalent metal cations $M^{III}_{1/2}M^V_{2/3}$ with $M^{III} = \text{Fe, In, Sc}$, heavier lanthanide elements and $M^V = \text{Nb, Ta}$ or combinations $M^{III}_{2/3}M^{VI}_{1/3}$ with $M^{III} = \text{Fe, In, Sc}$, heavier lanthanide elements and $M^{VI} = \text{W}$ or $M^{II}_{1/2}M^{VI}_{1/2}$ with $M^{II} = \text{Mg, Co, Ni}$ and $M^{VI} = \text{W}$ are used.

5. Piezoactor according to one of claims 2 to 2,
c h a r a c t e r i z e d i n t h a t

10 the compositions of the general formula $\text{Pb}^{II}_{1-x-y}\text{SE}^{III}_x\text{Cu}^{II}_y\text{V}'''_{x/2}(\text{Zr}_{0.54-z}\text{Ti}_{0.46+z})\text{O}_3$ corresponds with $0.01 < x < 0.05$ and $-0.15 < z < +0.15$ as well as $0 < y < 0.06$, with SE = a rare earth metal are provided, whereby a PbO surplus from 1 to maximally 5 molar-% is set.

15 6. Piezoactor according to one of claims 2 to 5
c h a r a c t e r i z e d i n t h a t
the green foils with electrode layers are coated with a copper powder-containing paste and stacked on top of each other and
20 subsequently laminated such that the result is an alternating sequence of green foils and Cu-electrode layers in the stack, which, being disposed opposite each other, alternately protrude and can be contacted in this manner.

25 7. Piezoactor according to one of claims 2 to 6,
c h a r a c t e r i z e d i n t h a t
the laminated stack is debindered, without air, at temperatures of up to 500°C with nitrogen, to which sufficient steam is added and which has a remaining oxygen partial
30 pressure which is compatible with metallic copper.

8. Piezoactor according to one of claims 2 to 7,
c h a r a c t e r i z e d i n t h a t

after debinding a sintering is carried out at approximately 1000°C in a steam-containing nitrogen atmosphere, the oxygen partial pressure of which is provided by adding a small amount of hydrogen according to the thermo-dynamic data of the steam-dissociation equilibrium such that the Cu/Cu₂O-equilibrium is not exceeded and the equilibrium oxygen partial pressure for the stability of the piezo-ceramic as compared to a reductive degradation does not fall below.

9. The piezoactor according to one of claims 2 to 8, characterized in that the sinter condensation in a hold time of 2 to 6 hours has lead to more than 96% of the theoretical density and a diffusion of copper atoms in the ceramic foil layer thereby simultaneously took place, which supported the grain growth to 1 to 10 µm at the sinter temperature.

10.. Piezoactor according to one of claims 2 to 9, characterized in that a higher layer thickness is chosen as layer thickness lead during the application of electrode layers, or a PZT ceramic modified with a CuO-addition with $y > 0$ is provided, in order to particularly prevent the decrease of the thickness of the interior electrode due to the indiffusion of copper into the ceramic.

11. Piezoactor according to one of claims 2 to 10, characterized in that an increase of the Curie-temperature by means of indiffusion of copper into the ceramic layer or right from the beginning by means of a specific addition of CuO to the raw material mixture is provided.

12. Piezoactor according to one of claims 2 to 22,

c h a r a c t e r i z e d i n t h a t
the piezoelectric characteristics of the PZT-ceramic modified
by indiffused copper or a CuO-addition by variation of the
Zr/Ti-ratio or a different suitable substitution on the B-
5 positions of the Perovskite-structure are adjusted to the
morphotropic phase boundary.

13. Piezoceramic component according to claim 1,
c h a r a c t e r i z e d i n b y
10 the characterizing feature of one of claims 2 to 12.

14. A method for producing a piezoceramic component in
monolithic multi-layer style with Cu-interior electrodes on
the basis of a ferroelectric Perovskite-ceramic ABO_3 of any
15 composition, preferably of the PZT-type $Pb(Zr_xTi_{1-x})O_3$,
c h a r a c t e r i z e d i n t h a t
a modification by mixed crystal formation by the assembly of
cations is provided on the A-positions as well as by
substitution of the B-cations by suitable other cations or by
20 combinations of cations.

15. Method for producing a piezoceramic component according
to claim 14,
c h a r a c t e r i z e d i n t h a t
25 for the substitution on the A-positions of the ferroelectric
Perovskite-ceramic, mainly of PZT type, bivalent metal cations
 M^{II} , such as Ba, Sr, Ca, Cu, or Bi or as rare earth metal Sc,
Y, La, of one of the Lanthanide elements which follow in the
periodic system or any combination of these elements is used
30 and thereby the combination with monovalent cations, such as
 Ag^I , Cu^I , Na^I or K^I is used.

16. Method for producing a piezoceramic component according
to claim 14 or 15,

c h a r a c t e r i z e d i n t h a t

for the partial substitution of the quadrivalent cations Zr and Ti on the B-positions of the ferroelectrical Perovskite ceramic, mainly of PZT-type, combinations of mono- and

- 5 quintvalent metal cations $M^I_{1/4}M^V_{3/4}$ with $M^I = \text{Na, K}$ and $M^V = \text{Nb, Ta}$ or bi- and quintvalent metal cations $M^{II}_{1/3}M^V_{2/3}$ with $M^{II} = \text{Mg, Zn, Ni, Co}$ and $M^V = \text{Nb, Ta}$ or tri- and quintvalent metal cations $M^{III}_{1/2}M^V_{2/3}$ with $M^{III} = \text{Fe, In, Sc}$, heavier lanthanide elements and $M^V = \text{Nb, Ta}$ or combinations $M^{III}_{2/3}M^{VI}_{1/3}$ with $M^{III} =$
10 Fe, In, Sc, heavier lanthanide elements and $M^{VI} = \text{W}$ or $M^{II}_{1/2}M^{VI}_{1/2}$ with $M^{II} = \text{Mg, Co, Ni}$ and $M^{VI} = \text{W}$ are used.

17. Method for producing a piezoceramic component according to one of claims 14 to 16,

15 c h a r a c t e r i z e d i n t h a t

the compositions of the general formula Pb^{II}_{1-x-}

$y\text{SE}^{III}_x\text{Cu}^{II}_y\text{V}'''_{x/2}(\text{Zr}_{0.54-z}\text{Ti}_{0.46+z})\text{O}_3$ corresponds with $0.01 < x <$
 0.05 and $-0.15 < z, +0.15$ as well as $0 < y < 0.06$, with SE =
a rare earth metal are used and furthermore a PbO-surplus from
20 1 to maximally 5 molar-% is set.

18. Method for producing a piezoceramic component according to one of claims 14 to 17,

c h a r a c t e r i z e d i n t h a t

- 25 green foils with electrode layers are coated with a copper powder-containing paste and stacked on top of each other and subsequently laminated such that the result is an alternating sequence of green foils and Cu-electrode layers in the stack, which, being disposed opposite each other, alternately
30 protrude and can be contacted in this manner.

19. Method for producing a piezoceramic component according to one of claims 14 to 18,

c h a r a c t e r i z e d i n t h a t

the laminated stack is debindered, without air, at temperatures of up to 500°C with nitrogen, to which sufficient steam is added and which has a remaining oxygen partial pressure which is compatible with metallic copper.

5

20. Method for producing a piezoceramic component according to one of claims 14 to 19,

c h a r a c t e r i z e d i n t h a t

after debinding a sintering is carried out at approximately

10 1000°C in a steam-containing nitrogen atmosphere, the oxygen partial pressure of which is adjusted by adding a small amount of hydrogen according to the thermo-dynamic data of the steam-dissociation equilibrium such that the Cu/Cu₂O-equilibrium is not exceeded and the equilibrium oxygen partial pressure for
15 the stability of the piezo-ceramic as compared to a reductive degradation does not fall below.

21. Method for producing a piezoceramic component according to one of claims 14 to 20,

20 c h a r a c t e r i z e d i n t h a t

the sinter condensation in a hold time of 2 to 6 hours has reached more than 96% of the theoretical density and a diffusion of Cu in the ceramic foil layer takes place at the same time, which supports the grain growth to 1 to 10 µm at

25 the sinter temperature which is comparatively low because it is predetermined by the melting point of the copper at 1083°C, and which leads to a positive compound between Cu-interior electrode and the piezoceramic.

30 22. Method for producing a piezoceramic component according to one of claims 14 to 21,

c h a r a c t e r i z e d i n t h a t

a decrease of the thickness of the interior electrode due to the indiffusion of copper into the ceramic is prevented in

that during the application of the electrode layers, a higher layer thickness is chosen as layer thickness lead during the application of the electrode layers, or a PZT ceramic modified with a CuO-addition with $y > 0$ is used.

5

23. Method for producing a piezoceramic component according to one of claims 14 to 22,

c h a r a c t e r i z e d i n t h a t

10 the increase of the Curie-temperature which can be achieved by means of indiffusion of copper into the ceramic layer or right from the beginning by means of a specific addition of CuO to the raw material mixture, is used in an advantageous manner.

24. Method for producing a piezoceramic component according to one of claims 14 to 23,

15 c h a r a c t e r i z e d i n t h a t

the piezoelectric characteristics of the PZT-ceramic modified by indiffused copper or a CuO-addition by variation of the Zr/Ti-ratio or a different suitable substitution on the B-positions of the Perovskite-structure are adjusted to the
20 morphotropic phase boundary.